HETEROGENEOUS REACTION OF ALKYLAMINES ON DICARBOXYLIC ACIDS RELEVANT TO SECONDARY ORGANIC AEROSOL FORMATION

A Thesis

by

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ABSTRACT

Secondary organic aerosols (SOA) are derived from non- and semivolatile oxidation products of volatile organic compounds (VOCs), and are suggested to cause adverse effects on human health, visibility, and climate. Organic acids are often found in SOAs, and the acid-base neutralization of these species by low molecular weight amines may result in the formation of stable low volatility aminium salt products contributing to the growth of SOAs and even alteration of the aerosol properties. Moreover, both laboratory and field studies suggest that atmospheric amines may exist as aminium salts following neutralization reactions with acidic species; however, the mechanisms involved in these processes are still uncertain.

In order to understand the mechanisms entailed in the growth of SOAs, the uptake of gaseous dimethylamine (DMA) and trimethylamine (TMA) on solid phase succinic acid and adipic acid was investigated by employing a laminar fast flow reactor coupled to an ion drift chemical ionization mass spectrometer (ID-CIMS). The heterogeneous uptake of amines on each acid was rapid and governed primarily by the steric effects of each amine and the acidity of each acid. The results show that acid-base reactions between organic acids and atmospheric amines could contribute to the formation of aminium carboxylate salts and in turn the growth of SOAs.

DEDICATION

This work is dedicated to my big sister Kimesha Allen.

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I would also like to give a special thanks to Dr. Alexei Khalizov for the guidance and encouragement he has given to me. Finally, I extend thanks to my family and friends.

NOMENCLATURE

SOA	Secondary Organic Aerosol
ID-CIMS	Ion Drift-Chemical Ionization Mass Spectrometer
DMA	Dimethylamine
MMA	Monomethylamine
TMA	Trimethylamine

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1. INTRODUCTION

Aerosols are suspensions of fine solids or liquids in the atmosphere, and are known to exist in sizes ranging from a few nanometers to several microns.[1]Atmospheric aerosols may exist in the form of primary aerosols, which are emitted directly into the atmosphere from natural sources (e.g. windblown plant particles, dust, sea spray, volcanic emissions, wildfires, etc.) or anthropogenic sources (e.g. biomass burning, industry, animal husbandry, etc.). [1] On the other hand, some pre-existing gaseous species in the atmosphere have the potential to undergo physical and chemical transformations to form secondary aerosols, a process known as new particle formation.[2] The new particle formation phenomenon not only pertains to the nucleation of atmospheric aerosols, but also the earliest stages of particle growth. Aerosol nucleation is essentially the formation of a molecular cluster that acts as a basis for the development of a new phase, i.e. the transformation of a molecule from gas to liquid to solid. Nucleation of new aerosol particles will typically begin with collisions between atoms or molecules in a pre-existing phase.[2]As the molecules collide, they gradually form larger more ordered particles. When considering the thermodynamics of the reaction, transforming from a less ordered to a more ordered phase would result in a decrease in both enthalpy and entropy. Therefore, the reaction would be exothermic and thermodynamically favorable according to the first law of thermodynamics. However, according to the second law of thermodynamics, the nucleation of the particle would be thermodynamically hindered by the entropy term, resulting in a free energy barrier that must be overcome before particle growth will become spontaneous.

The Kelvin effect also serves as a major limitation to the nucleation and growth of atmospheric nanoparticles, as the equilibrium vapor pressures above small particles are very high. However, a few species have been found to play important roles in the early stages of aerosol growth by forming stable low volatility products that minimize the curvature effect and promotes aerosol nucleation. Therefore, the nucleation rate of aerosols is directly related to the composition of the aerosols and the concentrations of the gaseous species participating in the event, in addition to the volatility and reactivity of the nucleating species.[2] The formation of stable clusters is paramount in the nucleation of atmospheric nanoparticles. Studies suggest that sulfuric acid, amines, and organics synergistically contribute to the growth of aerosols in their earliest stages, since nucleation due to sulfuric acid alone does not explain new particle formation events atmospherically.[3]

As a result of their various sizes and compositions, atmospheric aerosols have been concluded to decrease human visibility, and even cause adverse effects on human health. For instance, these particles cause respiratory and cardiovascular diseases in addition to exacerbating existing health conditions.[4,5] There is even found to be a correlation between particulate matter concentrations and the human mortality rate.[6,7] On the global scale, reports have also established that aerosols directly and indirectly perturb the Earth's climate by absorbing and scattering incoming solar radiation.[8] The indirect effects of aerosols are primarily attributed to atmospheric nanoparticles functioning as cloud condensation nuclei (CCN). Radiative forcing of aerosols accounts

for the greatest uncertainty when developing accurate climate models due to inadequate understanding of the properties, composition, and formation of these particles.[9]

1.1 Secondary Organic Aerosols (SOAs)

Organic species constitute a large fraction of aerosol particles,[10] ranging from 20-90% of the aerosol mass in the lower troposphere.[11] Organic matter may be emitted into the atmosphere directly (primary organic aerosols) or form in the atmosphere creating secondary organic aerosols (SOAs). Much of the organic matter found in SOAs is derived from the photo-oxidation of volatile organic compounds (VOCs), which are emitted from diverse natural and anthropogenic sources.[12,13] The products resulting from the photo-oxidation of VOCs are often comprised of hydroxyl, carbonyl, and carboxyl functional groups.[14,15] These species often have higher molecular weights than the reaction precursors,[16] and volatilities that are sometimes semi or non- in nature that facilitate transfer to the particle and condensed phases in addition to gas-particle partitioning of semivolatile species, and heterogeneous reactions.

Recently, Wang et al. investigated the contribution of several organic vapors to the nucleation of aerosol particles in a sulfuric acid-water binary system. The chosen vapors--2,4-hexadienal, glyoxal, and trimethylamine--were exposed to nanoparticles (2-20 nm) meanwhile the change in particle size was monitored using a nano-tandem DMA.[17] The size distributions of polydisperse sulfuric acid nanoparticles before and after exposure to 2,4-hexadienal showed evidence that the presence of organics caused a shift in the size distributions of particles larger than 4 nm. The authors believed that the growth was a result of heterogeneous reactions, resulting in the formation of low

volatility oligomers, polymers, and alkylaminium sulphates for 2,4-hexadienal, glyoxal, and trimethylamine, respectively.[19,20] While organic species are generally considered to play an integral part in the formation and growth of SOAs, the underlying mechanisms entailed in the nanoparticle growth processes are not well understood. However, it has been conjectured that particular organic compounds may participate in heterogeneous reactions, in which the products formed will expedite nanoparticle growth by overcoming the Kelvin barrier.[21]

1.2 SOAs: Organic Acid Interactions

Organic acids are important components of atmospheric aerosols,[22-27] where dicarboxylic acids are the most abundant type of organic acids, being found in the urban, suburban, rural, and polar atmospheres.[29-32] Dicarboxylic acids are known to contribute 1-3% of the total particulate carbon in urban and semi-urban areas and can reach near or above 10% in remote marine environments.[22,25,28,33] The general molecular formula for a dicarboxylic acid is HOOC-(CH_2)n-COOH where n is the number of carbons. Oxalic, malonic, and succinic acids are generally the three most abundant dicarboxylic acids in the lower troposphere, contributing to more than a half of the total diacid mass concentration.[24,25,33,34] Dicarboxylic acids may be emitted directly from anthropogenic (fossil fuel combustion, meat cooking) and biogenic (tropical forest environments, deciduous trees, coniferous trees, etc.) sources, or form through the photochemical conversion of precursors.[23] For instance, glutaric and adipic acids in the atmosphere are a result of the oxidation cyclohexene of with O_3,[35] and pinonic acid is formed from the

oxidation of α-pinene found in forest particulate matter via reactions with OH and O_3.[36,37]

Organic acids have been shown to play significant roles in the formation and growth of atmospheric particles.[38-40] The compositions of ambient nucleation mode aerosol particles in Tecamac, Mexico were measured using a TD-CIMS. The particles were 10-33 nm in diameter and exhibited the existence of carboxylic and hydroxy carboxylic organic acids.[41] The average ion molar ratios for organic species showed that these components could play a major role in the growth of ambient particles.[41] They may contribute to the formation and growth of SOAs by interacting with sulfuric acid-water binary systems,[42,43] forming strong heterodimers with sulfuric acid,[40] and condensing on to pre-existing particles due to their low volatilities.[44]

Growth by condensation is a commonly acknowledged mechanism for nanoparticle development in the atmosphere, and the condensation of low volatility organic acids is proposed to be a likely mechanism for atmospheric nanoparticle growth.[44] Since the saturation vapor pressures of organic trace gases were calculated to be quite large over nanometer sized particles,[21] condensation may likely include the formation of hydrogen bonds between the organic species and H_2SO_4 and/or H_2O comparable to that of sulfuric acid. Stable complexes have been concluded to form between mono- and dicarboxylic organic acids and sulfuric acid through double hydrogen bonding.[19] This interaction may even lead to a decrease in free energy and intensify the subsequent condensation of H_2SO_4 and H_2O positively charged and neutral

nanoparticles.[43,45] Unfortunately, there are very few laboratory studies that investigate the condensation of organic acids directly onto atmospheric nanoparticles.

Zhang et al. utilized a condensation particle counter (CPC) to evaluate the roles of several low-volatility organic acid vapors (e.g. benzoic, p-toluic, and m-toluic acids) when exposed to nanometer sized sulfuric acid aerosol particles produced in an aerosol chamber at 5 % RH. Following the addition of the low ppb level benzoic acid (0.1 and 0.04 ppb), an increase in aerosol concentration was observed that greatly exceeded that of sulfuric acid in both high and low concentrations alone (8×10^9 and 6×10^9 molecules cm^{-3}, respectively). The aerosol particle size distributions displayed a noticeable shift to larger size ranges, providing evidence that the organic vapors enhanced not only sulfuric acid aerosol nucleation but also the growth of these nanoparticles.[38] When plotting the particle concentrations versus the nucleation time, the nucleation rates of the organic acid/H_2O/H_2SO_4 nucleation systems demonstrated a pronounced enhancement with at 5% RH, which lead them to believe that organic acid/H_2SO_4 interactions result in the formation of heteromolecular complexes, increasing the stability of the nanoparticle and therefore reducing the nucleation barrier and enhancing nanoparticle growth.[38] However, when the concentrations of the organic acids were not present, increasing the concentrations of H_2SO_4 added also displayed an increase in the aerosol nucleation rate, showing the dependence of nucleation on the H_2SO_4/ H_2O binary system. In 2009, Zhang et al. performed a similar study in which cis-pinonic acid/H_2O/H_2SO_4 nucleation was observed in an aerosol chamber to serve as a simulation for biogenic aerosol nucleation over forests. Particle size distributions

determined by a nano-differential mobility analyzer (DMA) again demonstrated the influence organic acid in the nucleation and growth of aerosol particles.[39] Nucleation rates were also enhanced with the increased concentrations of the organic acid, but also when sulfuric acid increased with the organic acid concentrations remaining constant. The results of both studies showed that differentiating the contribution of organic acids and sulfuric acid to the nucleation and growth of atmospheric particles without supplementary chemical analysis may prove to be difficult.[39] Therefore, the chemical compositions of the nucleated nanoparticles were determined by way of a thermal desorption-ion drift-chemical ionization mass spectrometer (TD-ID-CIMS). The results obtained showed that H_2SO_4 and H_2SO_4-H_2SO_4 dimers were more abundant in the 3-13 nm sized nucleated particles than cis-pinonic acid and cis-pinonic acid-H_2SO_4 heterodimers with a ratio of 1000:1 even at comparable gas phase concentrations.[39]

Condensation on nanoparticles is significantly limited because of the elevated equilibrium vapor pressures from the Kelvin curvature effect. Sulfuric acid condensation on newly nucleated particles is facilitated by the simultaneous condensation of water, which stabilizes the particle preventing evaporation. On the other hand, the condensation of low solubility organic species, such as cis-pinonic acid, on to newly nucleated particles is limited by the acid's hydrophobic properties. Therefore, the earliest stages of aerosol growth to detectable sizes can be attributed to the formation of stabilized sulfuric acid-water complexes, while the organic acids catalyze subsequent growth via the formation of stable complexes with sulfuric acid. The notable increase in sulfuric acid aerosol particle sizes in the presence of organic acids is possibly because the enhanced

nucleation rates produce nanoparticles more rapidly allowing additional growth time for the particles.[38,39] Because the enhancement from organics on the sulfuric acid-water binary system is comparable to that when ammonia is present,[43,46] aerosol growth in the presence of organics may be the cause of the elevated concentrations of aerosols measured in polluted urban areas where VOCs exist in high concentrations.[47-49]

1.3 SOAs: Alkylamine Interactions and Chemistry

Atmospheric amines are also important organic components of atmospheric aerosols, being found in aerosol particles at various locations all over the world.[50] They may even provide up to 20% of organic content in ambient particles.[51] Amines are ammonia derivatives in which hydrogen atoms are replaced by carbon-based substituents, such as alkyl or aryl groups. Low molecular weight aliphatic amines (1-6 carbons), such as methylamine (MMA), dimethylamine (DMA), and trimethylamine (TMA), are the most abundant amines atmospherically with global emission values of 83±26, 33±19, and 169±33 Gg N y^{-1}.[52]Alkylamines are frequently emitted in the atmosphere, originating from biogenic and anthropogenic emissions not limited to biomass burning, animal husbandry, sewage treatment, and oceanic organisms.[50]

Computational studies were performed which demonstrated that amines also have the ability to form strong hydrogen bonds with sulfuric acid that can assist in overcoming the nucleation free energy barrier, even more so than ammonia,[53,54] a substance has been shown to increase binary nucleation rates, and neutralize sulfuric acid to form ammonium salts, contributing to the growth and stabilization of aerosols.[2,55]

Laboratory studies were also performed in order to ascertain the effects of atmospheric amines on new particle formation in comparison to ammonia.[56-58]

Yu and coauthors performed a nucleation in which the ability of amines and ammonia to enhance H_2SO_4/ H_2O particle nucleation were expressed in terms of an enhancement factor (EF), which was calculated by taking the ratio of the total particle number concentrations measured with and without the addition of each base via a particle size magnifier (PSM).[58] The results of the study showed that sulfuric acid particles with diameters larger than 1nm were enhanced by DMA (0.7 ppbv) at constant RH of 32 and 18%. The enhancement initially showed dependence on the DMA present, but later transitioned to a dependence on the sulfuric acid concentrations. This shows evidence that DMA is involved in the nucleation of atmospheric aerosols, while sulfuric acid is the key nucleation precursor that drives the formation of sub-3nm particles, even in the presence of ppb level ternary bases. Moreover, the formation of particles were enhanced in the presence of amines two orders of magnitude higher than ammonia when exposed to the sulfuric acid particles with diameters greater than 2 nm (7×10^6 molecules cm^{-3} and RH of 32%). The enhancement by amines occurred in order of basicity, which suggests that acid-base reactions have key importance of in the nucleation of sulfuric acid aerosol particles.

Amines also have the ability to enhance the nucleation rate of sulfuric acid aerosols, as shown by Erupe et al.[56] A chemical ionization mass spectrometer (CIMS) was utilized to detect the change in nucleation rate of the sulfuric acid aerosols at increasing concentrations ($5 \times 10^6 - 1 \times 10^8$ molecules cm^{-3}) within an RH range of 12-

41% in the presence of TMA at concentrations between 180-1350 pptv (from 4.5 x 10^9 to 3.4 x 10^{10} molecules cm^{-3}). With 480 pptv TMA present, the nucleation rate J increased in comparison to the nucleation rate when TMA is absent. The reported sulfuric acid particles present in the nucleating particles decreased from 4-6 without TMA to 4-5 with TMA depending on the RH value, implying that only one TMA molecule is present in the critical nucleus, similar to the addition of ammonia. Since atmospheric amine concentrations can range from 10^8-10^9 molecules cm^{-3} or higher depending on the proximity of sources,[50] it is probable that amines may play a central part in atmospheric nucleation of sulfuric acid and water. Although amines have been shown to enhance aerosol nucleation in the presence of sulfuric acid, the means by which this phenomenon occurs is currently unknown. The nucleation could be enhanced as a result of overcoming the Kelvin effect via the formation of nonvolatile products, or enhancement could be due to overcoming the free energy barrier through the formation of strongly hydrogen-bonded clusters with sulfuric acid, since there is currently no means to distinguish the two processes.

Atmospheric amines have been implicated to not only exceed the new particle enhancement of ammonia,[56-58] but also play important roles in the growth of secondary aerosols. Although the global emission of amines is orders of magnitude lower than ammonia (50000±30000 Gg N y^{-1}),[59] amines have the potential to participate in multiphase reactions within bulk aerosol phases due to their high solubility and basicity. Among the suggested bulk aerosol reaction pathways are carbonyl-amine interactions, considering that carbonyl containing organic compounds are the most abundant in the

atmosphere, being emitted directly or forming as a result of the oxidation of organic compounds. Primary and secondary amines can undergo reactions with the carbonyl groups to form imine and enamine compounds.[60] For instance, particle and solution phase reactions between glyoxal and MMA were measured.[61] Solutions of glyoxal trimer dehydrate and 40% w/w MMA were prepared then dried in air for analysis of the bulk phase, or dried with humidified nitrogen to simulate cloud droplet evaporation. The results were analyzed using ESI-MS and high resolution TOF-MS. The result showed that the amines may act as a nucleophile and react with the glyoxal aldehyde to produce hydrated imines as the droplet dried. These imine compounds could either form imine dimers, imidazole compounds, or continue to dehydrate. The protonated imine dimers could incorporate varying amounts of water, resulting in 2nd generation imine products.[61] The imine dimers could then potentially react to form oligomers as the droplet continued to dry and evaporated excess MMA. This indicates that amines contribute to the increase in aerosol mass.[61] Moreover, field studies have identified high molecular weight species in urban aerosols (Shanghai, China) are composed of a large fraction of organic species containing carbon–nitrogen bonds.[62] It is suggested that amines react with carbonyl containing compounds to form organic salts, which could serve as an important mechanism for the formation of organic nitrogen in aerosols.[62] It is highly probable that the reactions will be acid-catalyzed since multiple organic and inorganic acidic species are common in the atmospheric particle phase.

Particulate amines may also react with gas-phase oxidants, such as ozone and OH radicals. The products will consequentially be more oxidized have higher or lower MW,

contributing to aging of organic aerosols.[63] Zahardis et al. investigated the oxidation of particulate amines octadecylamine (ODA) and hexadecylamine (HDA) by ozone using a flow reactor based experiment utilizing photoelectron resonance capture ionization aerosol mass spectrometry (PERCI-AMS).[64] Direct oxidation of amines yielded organic nitrogen compounds, while mixed oxidized sample particles of amines and oleic acid produced imines and amides which could contribute to the transformation of aerosol particles.[64]

Heterogeneous reactions between condensed phase inorganic/organic acids have been recently recognized as an important mechanism for the production of organic nitrogen in the form of alkylaminium salts, contributing to the mass of SOAs.[65-67] For example, amines have been shown to neutralize condensed sulfuric acid to form alkylaminium sulfates.[65] The heterogeneous reactions of DMA, TMA, and MMA with sulfuric acid (59-82 wt%) were studied at 243 and 283 K in order to ascertain the function of amines in the growth of atmospheric aerosols through the formation of alkylaminium sulfates. Kinetics measurements of the reactions were examined in a low-pressure fast flow reactor coupled to an ion drift-chemical ionization mass spectrometer (ID-CIMS).[65] The uptake for all three amines was completely irreversible, resulting in uptake coefficients (γ) in the range of 2.0×10^{-2} to 4.4×10^{-2}, increasing with an increase in sulfuric acid concentration. The results infer that the heterogeneous reactions of amines contribute efficiently to the growth of SOAs through acid-base neutralization.

Although amines react proficiently with sulfuric acid to form stable clusters, amines exist in concentrations several orders of magnitude lower than that of ammonia,

which would imply that ammonia would be more likely to participate in heterogeneous reactions with sulfuric acid. However, amines have the ability to displace ammonia on sulfate and nitrate aerosols to form more stable alkylammonium salts.[66,68,69] Lloyd and coauthors studied the reaction of TMA vapor when exposed to a polydisperse distribution of ammonium nitrate particles, 20-500 nm in diameter, using a flow tube reactor coupled to a laser desorption (LD) electron ionization (EI) TOF-AMS.[68] In the absence of TMA vapor, ion peaks at m/z 17, 30 and 46 were observed indicating the presence of NH_3^+, NO^+, and NO_2^+, respectively, which are commonly produced by a pulsed IR laser beam. However, when exposed to a high concentration of TMA vapor from a 45 wt% solutions, a complete exchange of ammonia for TMA was observed based on the absence of m/z 17 and the additions of m/z 58 and 59 (TMA).[68] At a lower TMA vapor concentration (~500 ppb and a 23 s reaction time), a partial exchange of TMA was observed, and the initial reactive uptake coefficient was estimated to be 2 x 10^{-3} at 20% RH.[68] Furthermore, the heterogeneous reactions between gaseous MMA, DMA, and TMA by ammonium sulfate and ammonium bisulfate were studied at 293 K using a low pressure fast-flow reactor coupled to an ID-CIMS.[66] The reaction between the alkylamines and ammonium bisulfate resulted in a completely irreversible acid-base neutralization reaction similar to that of sulfuric acid and amines[65] with no increase in ammonia signal. However, all three amines exhibited a displacement reaction with ammonium sulfate in which ammonia was released, indicated by an increase in a protonated ammonia signal.[66] The initial uptake coefficients for this reaction were on the

order of 2.6 x 10^{-2} to 3.4 x 10^{-2} and 6.0 x 10^{-3} to 2.3 x 10^{-4} for the steady state, decreasing with increasing methyl groups.[66]

Because several studies suggest that alkylamines exist in the particle phase as alkylaminium salts,[66-69,41] it is likely that the acid-base neutralization of prevalent dicarboxylic acids and low molecular weight amines will also result in the formation of low-volatility aminium carboxylate salts in aerosols.[70] In 2012, Lui et al. investigated the heterogeneous uptake of MMA, DMA, and TMA at 298 K by citric and humic acid utilizing a Knudsen cell reactor coupled to a quadrupole mass spectrometer.[67] The acid base reaction between the amines and the organic acids were confirmed resulting in observed uptake coefficients from 7.31±1.13 x 10^{-3}, 6.65±0.49 x 10^{-3}, and 5.82±0.68 x 10^{-3} independent of sample mass for amines on citric acid for MMA, DMA, and TMA respectively.[67] However, the uptake coefficients for amines on humic acid increased linearly with sample mass. While steric effects governed the reactivity between amines and the organic acids, citric acid demonstrated a higher reactivity than humic acid since it had a stronger acidity.[67] Therefore, organic acids could potentially play a role in nanoparticle growth by heterogeneous reactions with gas-phase alkylamines and sulfuric acid, rather than solely influence particle growth by direct condensation into the existing particles. Additionally, Smith and co-authors utilized a TD-CIMS to analyze nanoparticle compositions from the US, Mexico and Finland, and confirmed the presence of alkylaminium carboxylate salts.[41] TD-CIMS observations of a NFP event at an urban site in Tecamac, Mexico indicated the existence of aminium salts in 8-10 nm particles, contributing to ~47% of the detected ions. Particle analysis at a remote forested

(Hyytiala, Finland) and rural sites (Boulder, CO) exhibited aminium ion ration from 10-35%. The very presence of aminium salts in newly formed particles indicates that they may play an integral role in the development of secondary aerosols.[41]

Although amines have been found to play an important role in the formation and growth of SOAs through heterogeneous and multiphase reactions with organic and inorganic compounds, very little is still known about the affects that the reaction products will have on the properties of the aerosols. However, recent laboratory studies have investigated the affects of alkylaminium sulfates on the hygroscopicity, stability, and optical properties of the resulting organic aerosol particles.[41,71,72] Qui et al. measured the properties of five alkylaminium sulfates using a tandem differential mobility analyzer (TDMA) and an aerosol particle mass analyzer.[71] The AAS aerosols exhibited a monotonic growth in the presence of increasing RH (10-90%) with no sign of a well-defined deliquescence point, suggesting that AAS absorb water even at low RH. In comparison to the hygroscopic growth of AASs, ammonium sulfate (AS) had a clear deliquescence point at around 80% RH, but upon mixing with AASs, the deliquescence point corresponding to AS was lowered considerably, decreasing even lower with high AASs concentrations.[71] This result clearly demonstrates the impact that AASs have on the hygroscopic behavior of aerosol particles.[71] The thermostability of each AAS particle was also assessed from 25-200 ºC and compared to that of AS. All of the AAS volatized rapidly between 130-170ºC comparable to AS, but monomethylaminium sulfate (MMAS) volatized at a temperature much lower than determined. Therefore, the transition from AS to AAS must lead from a previously crystalline phase to that of an

amorphous phase, which improves water uptake and may enhance direct and indirect climate forcing.[71] Moreover, Lavi et al. concluded that alkylaminium carboxylate salts yielded from organic acid-base reactions have high thermal stability and low volatility.[73] The vapor pressure of alkylaminium dicarboxylate salts was concluded to be ~10^{-6} Pa, lower than their precursor acids, with vaporization enthalpy ranging 73-134 kJ mol^{-1}. Alkylaminium monocarboxylate salts also show high thermal stability greater than the dicarboxylate salts, have been found to be protic ionic liquids at room temperature (RTPILs), and are more hygroscopic than ammonium sulfate (AS).[73] It is likely that internally mixed particles containing highly hygroscopic alkylaminium carboxylate salts, such as alkylaminium acetate and propinonate, will enhance the hygroscopic nature of organic aerosols, influencing the optical properties.[73]

Additionally, the hygroscopicity and optical properties of AASs were investigated using a hygroscopicity tandem differential mobility analyzer coupled to a cavity ring-down spectrometer with a nephelometer; the light extinction and scattering cross sections of 150 nm ethylaminium sulfate (EAS), diethylaminium sulfate (DEAS) and triethylaminium sulfate (TEAS) were measured from 2-85% RH.[72] The measure light extinction and scattering cross sections at 2% RH displayed a small yet distinguishable absorption cross section, which is typically not seen in AS aerosols.[74] As the RH increased (30-85 % RH), the absorption cross section began to become depressed due to and increase in the transparency of the aerosol and the increase in particle size.[72] Therefore, the extinction of AASs is dominated by scattering under high RH, but may exhibit absorptive properties under dry conditions.

Although many studies of SOAs have focused primarily on new particle formation (gas-to-particle conversion) and gas to particle partitioning mechanisms,[4] recent laboratory investigations show that heterogeneous reactions may contribute greatly to the aerosol formation and growth processes.[65,67,71,75,76] In this study, the growth of SOAs was investigated by studying the heterogeneous uptake of alkylamines by particle phase succinic and adipic acids. The species were chosen due to their atmospheric prevalence, solubility, and low vapor pressure (Tables 1 and 2). The heterogeneous reaction kinetics were expressed as uptake coefficients, γ, describing the probability in which gas phase amines will be irreversibly lost due to collisions with the stationary acid particles. The resulting kinetic data will allow us to gain insight into whether the acid-base neutralization reactions are feasible and occur at a rate that expedites the growth of new and existing aerosols.

Table 1. Physical and Chemical Properties of Succinic Acid and Adipic Acid

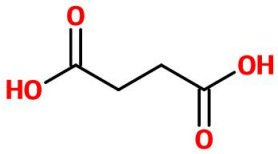
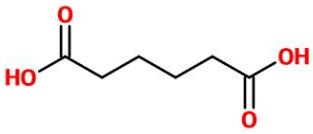
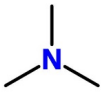
	Succinic Acid	Adipic Acid
		
Molecular Weight	118.09 g/mol	146.14 g/mol
[77]Solubility in H_2O, 25°C	8.3 x 10^4 mg/L	3.2 x 10^2mg/L
[77]Vapor Pressure, 30°C	6.90 x 10^{-7} torr	1.50 x 10^{-7} torr
pK^a (pKa_2)	4.19 (5.48)	4.43 (5.41)

Table 2. Physical and Chemical Properties of Alkylamines

		Molecular Weight	[78]VaporPressure, (20°C)	[79]pKb
DMA		45.08 g/mol	1.28x10^3 torr	3.36
TMA		59.11 g/mol	6.88x10^3 torr	4.24

2. MATERIALS AND METHODS

2.1 Heterogeneous Uptake Measurements

The heterogeneous reactions were studied using a low-pressure fast flow reactor coupled to an ion-drift chemical ionization mass spectrometer (ID-CIMS) (Figure 1). The ID-CIMS system entails a corona discharge ionization source, which is used to create positively charged reagent ions. The ions then react with the amine molecules in the drift tube followed by analyses by a quadrupole mass spectrometer. The flow reactor utilized a moveable injector, which facilitated alkylamine exposure to the organic acid samples. The flow reactor was coated with a layer of halocarbon wax to minimize the loss of amines to the reactor wall.[80] High purity compressed helium was employed as the carrier gas, and all gas flows were monitored using calibrated electronic mass flow meters (Millipore Tylan 260 series). The combined gas flows exhibited flow velocities within 513-588 cm s^{-1}. Table 1 gives the chemical and physical properties of all chemical species employed in this study. Pure DMA and TMA anhydrous gases (Aldrich, 99%) were diluted with ultra-high purity He by a two-step dilution. The dilution process entailed respectively adding alkylamines to a 2 L Pyrex bulb until an internal pressure ~2 torr was reached. The bulb was then pressurized to ~200 torr with He. The resulting mixture was then depressurized to ~3 torr, and then pressurized with He to ~375 torr. The final dilution resulted in a mixing ratio of ~80-90 ppm. Because the alkylamine gases did not stream from an online source, signal loss could be observed over the course of a single trial. To keep this loss at a minimum, the amine bulbs were replenished following about six independent experiments.

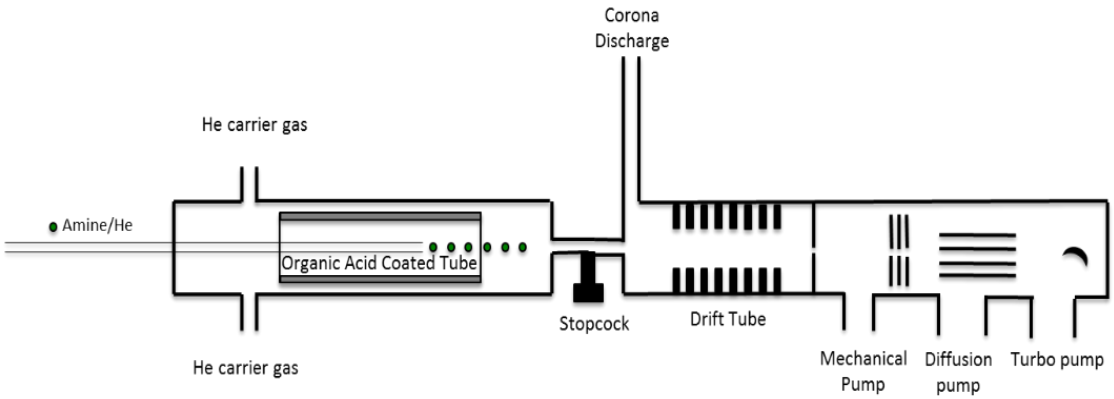


Figure 1. Diagram of a low-pressure fast flow reactor coupled to an ID-CIMS.

A 12.5 cm sandblasted glass cylinder with an inner radius of ~0.82 cm was coated with a 10-25 wt. % succinic and adipic acid (Sigma-Aldrich) solutions, respectively (Figure 2). Because succinic acid has a low solubility in water, the succinic acid solution was warmed to medium heat in order to create the saturated acid solution. The sandblasted glass cylinder was held vertically as the acid solution was drawn through the cylinder by a vacuum line connected by a critical orifice. The organic acid coated cylinder was oriented in a horizontal position then dried by slowly rotating in ambient air. The dried cylinder resulted in a crystalline acid layer several milligrams in thickness. The independent uptake experiments were performed under dry conditions at a 298 K at an average flow reactor pressure between ~1.4-1.5 torr.

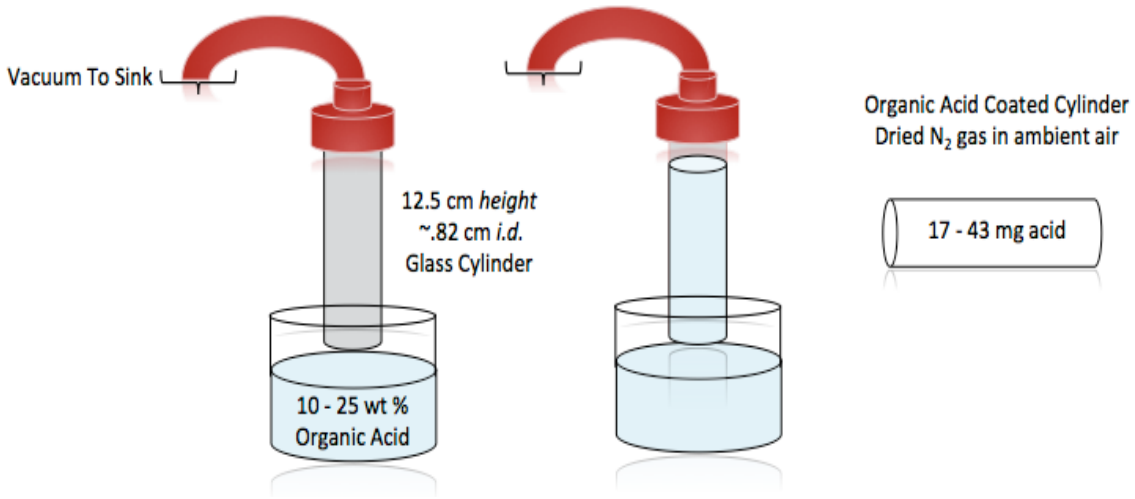


Figure 2. Diagram of organic acid cylinder coating procedure.

Single ion monitoring of the protonated alkylamine signals were performed using a proton transfer ionization scheme,

$$A + H_3O^+ \rightarrow AH^+ + H_2O \quad (1)$$

where A and AH^+ represent the un-protonated and protonated forms of the alkylamine respectively. The $[H_3O^+]$ reagent ion was produced by flowing charcoal filtered ambient air into a corona discharge ionization source. The DMA gas was monitored at its protonated peak *m/z* 46, and TMA was monitored at its protonated peak *m/z* 60. The hydronium ion $[H_3O^+]$ was monitored at *m/z* 19 in order to account for any fluctuations in the amine signal due to an unstable reagent ion flow (Figure 3).

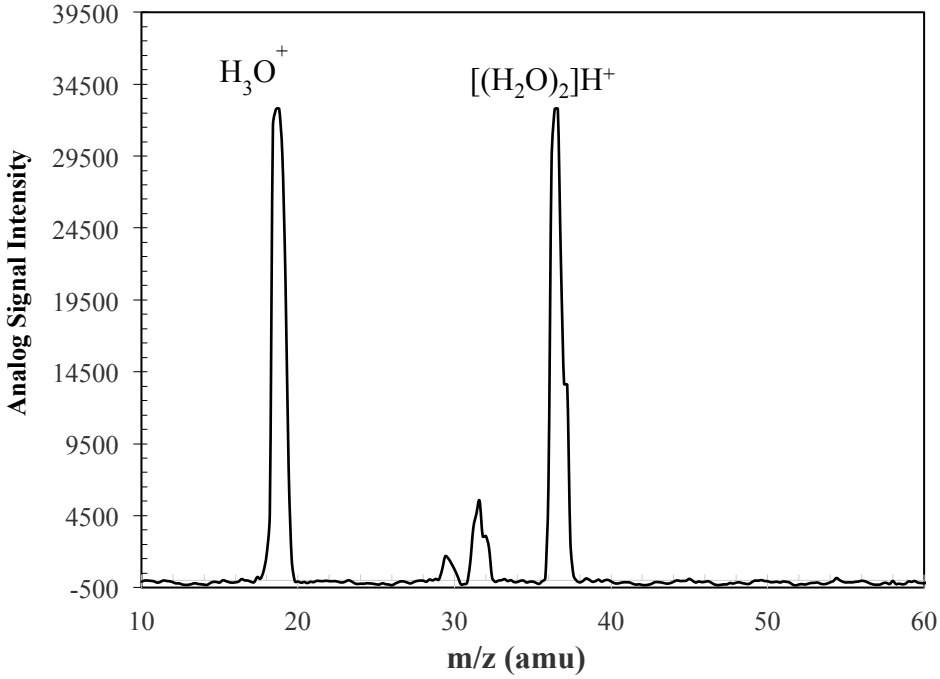


Figure 3. Positive mode mass spectral profile of the reagent ion H_3O^+ (m/z 19).

The heterogeneous kinetics of the alkylamine loss were expressed as the initial, γ_0, and steady state, γ_{ss}, uptake coefficients by employing equation (2)

$$\gamma = \frac{2rk_r}{\omega + rk_r} \tag{2}$$

where r is the radius of the sample tube, ω is the mean thermal speed, and k_r represents the pseudo-first order rate constant.[81] The first order rate constant k_r was calculated from the equation,

$$\frac{1}{k_{obs}} = \frac{1}{k_{diff}} + \frac{1}{k_r} \tag{3}$$

where k_{obs} is the observed first order rate constant, and k_{diff} is the rate constant due to the gas phase diffusion of amines to the reactor wall (4).[82]

$$k_{diff} = \frac{3.66 D_{amine/He}}{r^2} \quad (4)$$

Gas phase diffusion corrections were applied[83] and diffusion coefficients were estimated according to.[84] The observed first order rate constant, $k_{obs,}$ was given by equation (5),

$$k_{obs} = \frac{u}{l} \ln\left(\frac{I_o}{I_t}\right) \quad (5)$$

where u is the combined carrier flow velocity, l is the length of the sample tube that has been exposed to alkylamines, and I_o is the initial signal intensity of the either amine; I_t is the intensity of the amine signal at a given time.[66] The total amine signal was corrected for background and unstable amine flow before calculations were performed.

2.2 Alkylamine Probe Depth

Recent works illustrate the various physical processes that are implicated in heterogeneous uptake, including penetration of the aerosol particle.[84,85] When considering the total uptake of the alkylamine gas, the extended exposure period will allow sufficient time for the gas phase particles to not only saturate the surface of the acid coating, but also penetrate. Such a phenomenon was observed for the uptake of gaseous alkylamines by solid humic acid using a Knudsen cell reactor.[67] In order to ascertain whether the amine molecules exhibit such behavior when exposed to the dicarboxylic acid coatings, the monolayer fractions of reacted succinic acid and adipic

acid were estimated. In order to approximate these values, the number of organic acid molecules per unit area (A_{OA}) was initially calculated by employing equation (6), where ρ and M are the density (g cm^{-3}) and molecular weight (g mol^{-1}) of the respective organic acids, and N_A is Avogadro's number. The results of equation (6) and the surface area of the sample cylinder were multiplied to give the estimated number of acid molecules available for uptake per monolayer of acid.

$$A_{OA} = \sqrt{\left[\left(\frac{\rho \cdot N_A}{M}\right)^{\frac{1}{3}}\right]} \quad (6)$$

The total amine molecules lost during uptake were estimated by converting the temporal profile of either protonated amine into a plot of the molecular flow rate (molecules s^{-1}) versus time (s). The area of the uptake profile was then calculated resulting in the total number of amine molecules taken. Assuming that amines and dicarboxylic acids react in a 2:1 ratio, the monolayer fraction of the dicarboxylic acid reacted was determined by taking the ratio of the approximate number of acid molecules reacted (half of calculated amine molecules) to the number of exposed acid molecules available based on the injector distance.

3. RESULTS AND DISCUSSION

3.1 Uptake of Alkylamines on Succinic Acid and Adipic Acid

The heterogeneous uptake of gaseous DMA by succinic acid is shown in Figure 4. Once the protonated alkylamine signal had stabilized, the moveable injector was withdrawn so that the succinic acid coating was exposed to the alkylamine gas. Figure 4 shows the loss in DMA signal intensity upon exposure to 0.7-4.7 cm of the succinic acid coating. Upon immediate exposure to the sample surface, the DMA signal demonstrated an initial plunge around 30% of the original intensity (Figure 4a). Following the rapid initial interaction with the succinic acid coating, the amine signal began to recover asymptotically for ~200 s before gradually returning to ~10% of it's original position, reaching a steady state. However, as the injector distance increased (Figures 4b-e), the change in DMA signal loss increased as well, concluding with a maximum initial decrease in amine signal as large as ~80% (Figure 4e). The signal recovered slowly for ~800s before returning to a steady state, about 25% of initial signal intensity. Immediately following ~300 s of stabilization, the alkylamine exposure was terminated by returning the moveable injector to its initial position, which resulted in an abrupt increase in the DMA signal intensity observed in all five spectra, then a gradual decrease of the amine signal to about of the original intensity.

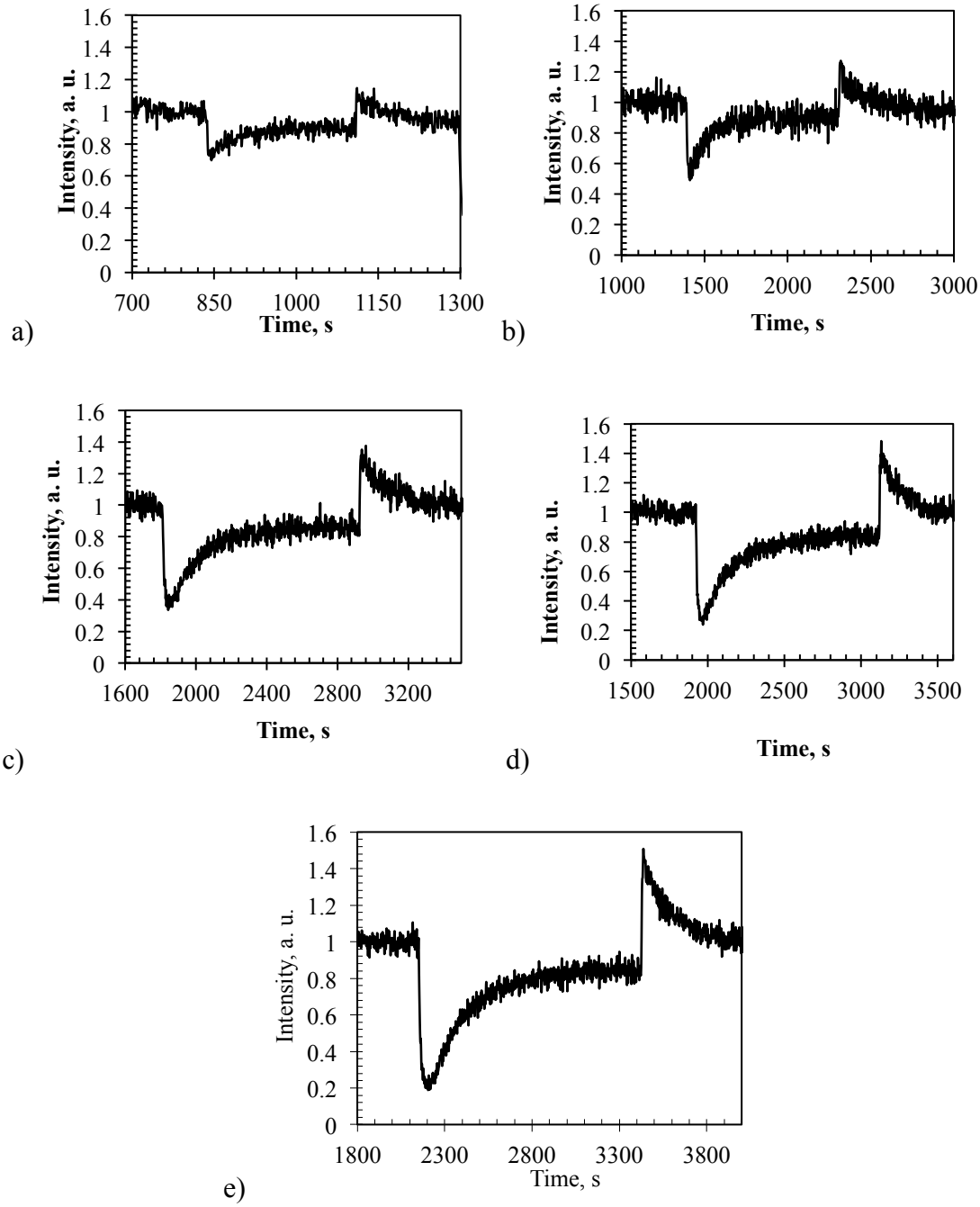


Figure 4. Normalized selected ion mass spectral profiles of $[DMA]\cdot H^+$ (m/z 46) when exposed to a) 0.7 cm b) 1.7 cm c.) 2.7 cm d.) 3.7 cm e.) 4.7 cm of a 43 mg succinic acid coating respectively at 298 K and ~1.4 torr.

The features shown by each profile imply that several processes occur between the alkylamine and the sample surface. The initial decay in amine signal could be attributed to the alkylamines contacting easily accessible sites on the surface of organic acid, such as steps and defects. The asymptotic recovery observed following the initial contact indicates that the succinic acid coating was not completely saturated with amines, therefore the uptake of amine may be limited by the diffusion of amines to the sample. On the other hand, the subsequent stabilization of the amine signal can be attributed to the amines saturating the entire surface of the acid coating, leaving no available acid molecules to uptake the remaining amines.

Once the injector was slid downstream, there was an abrupt increase in amine signal. This phenomenon implies that some amine molecules had been physically adsorbed on the succinic acid surface and were consequentially released to contribute to the existing amine signal. Several uptake measurements were conducted over the same sample surface, resulting in uptake comparable to an unreacted surface each time. This shows that not all of the succinic acid reacts upon exposure. Moreover, the desorption peak appeared to have a smaller area than that of the uptake curve, concluding that a large fraction of the gas phase amines were irreversibly lost due to reactive uptake, while the remaining fraction of the DMA signal lost was a result of the physical adsorption.

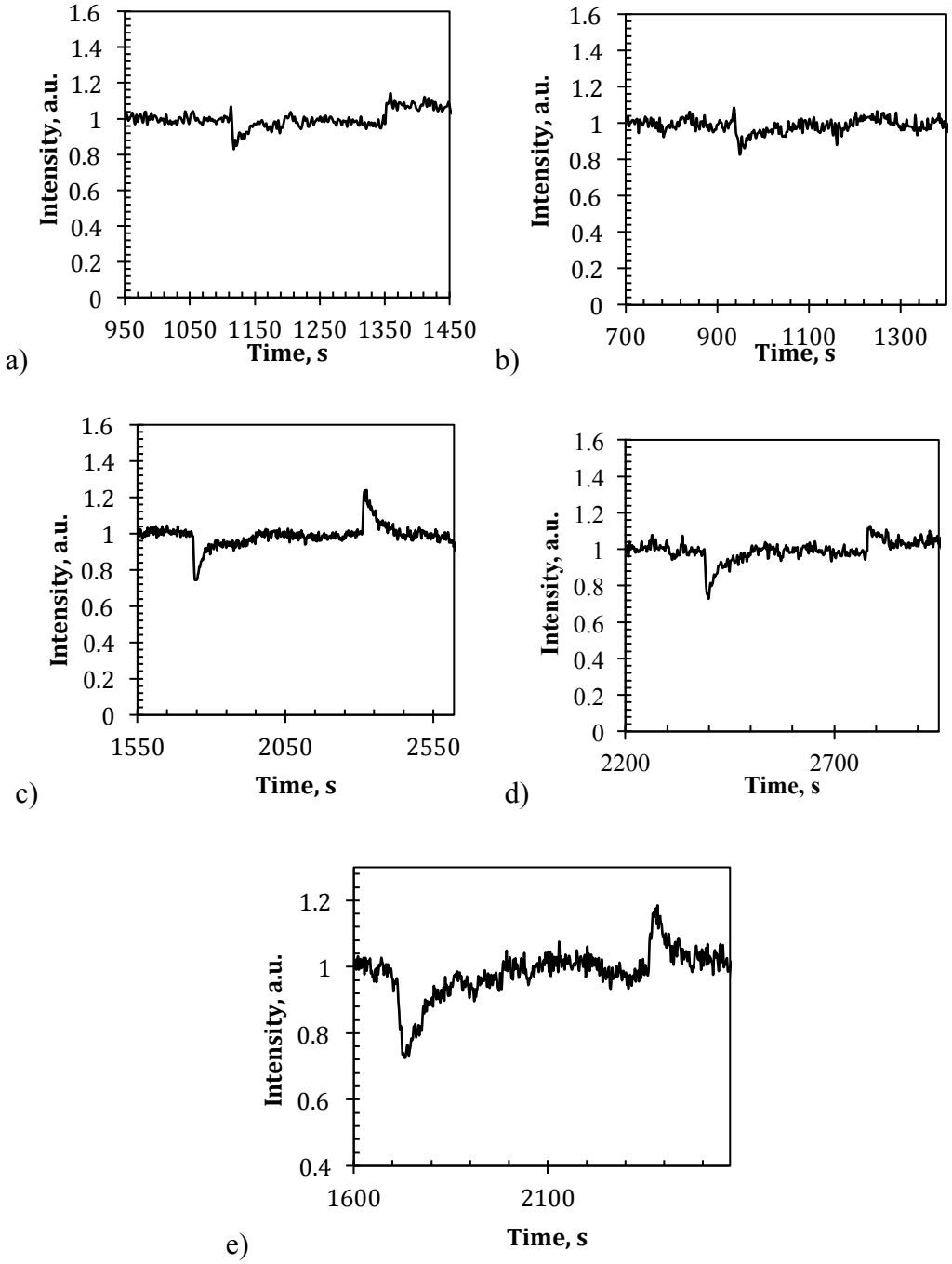


Figure 5. Normalized selected ion mass spectral profile of $[DMA]\cdot H^+$ (m/z 46) when exposed to a) 1.0 cm b) 2.0 cm c.) 3.0 cm d.) 4.0 cm e.) 5.0 cm of a 43 mg adipic acid coating respectively at 298 K and ~1.6torr.

Figure 5 depicts the loss in DMA signal intensity upon exposure to 1.0-5.0 cm of an adipic acid coating. The DMA signal experienced a rapid decay just as with succinic acid. However, upon exposure to the sample surface, the DMA signal demonstrated an initial plunge of only ~15% of the initial amine signal intensity (Figure 5a). Following the rapid initial interaction with the adipic acid coating, the amine signal began to recover for ~10 s until reaching a steady, returning to ~5% of it's original position. As with succinic acid, the change in DMA signal loss increased with the injector distance (Figures 5b-e), resulting in a maximum initial decrease in amine signal of about ~30% (Figure 5e). The amine signal recovered asymptotically for ~250 s before being restored to about 5% of initial signal intensity. Immediately following ~300 s of stabilization, the alkylamine exposure was terminated by returning the moveable injector to its initial position, resulting in a minimal increase in the DMA signal intensity. The increase in amine signal was comparable to the loss during initial uptake. The signal then quickly decayed to the initial amine intensity.

The uptake profiles for DMA on adipic acid share similar features with the signal loss and recovery shown in Figure 4. However, the uptake of amines by adipic acid for the initial and steady state are not as pronounced, and the area of desorption signal was comparable to that shown by the uptake signal loss. The features in the adipic acid profiles suggest that accommodation dominates the uptake; therefore, the amines likely adsorb to the surface of the adipic acid coating at a more rapid rate than reaction, and then are quickly released.

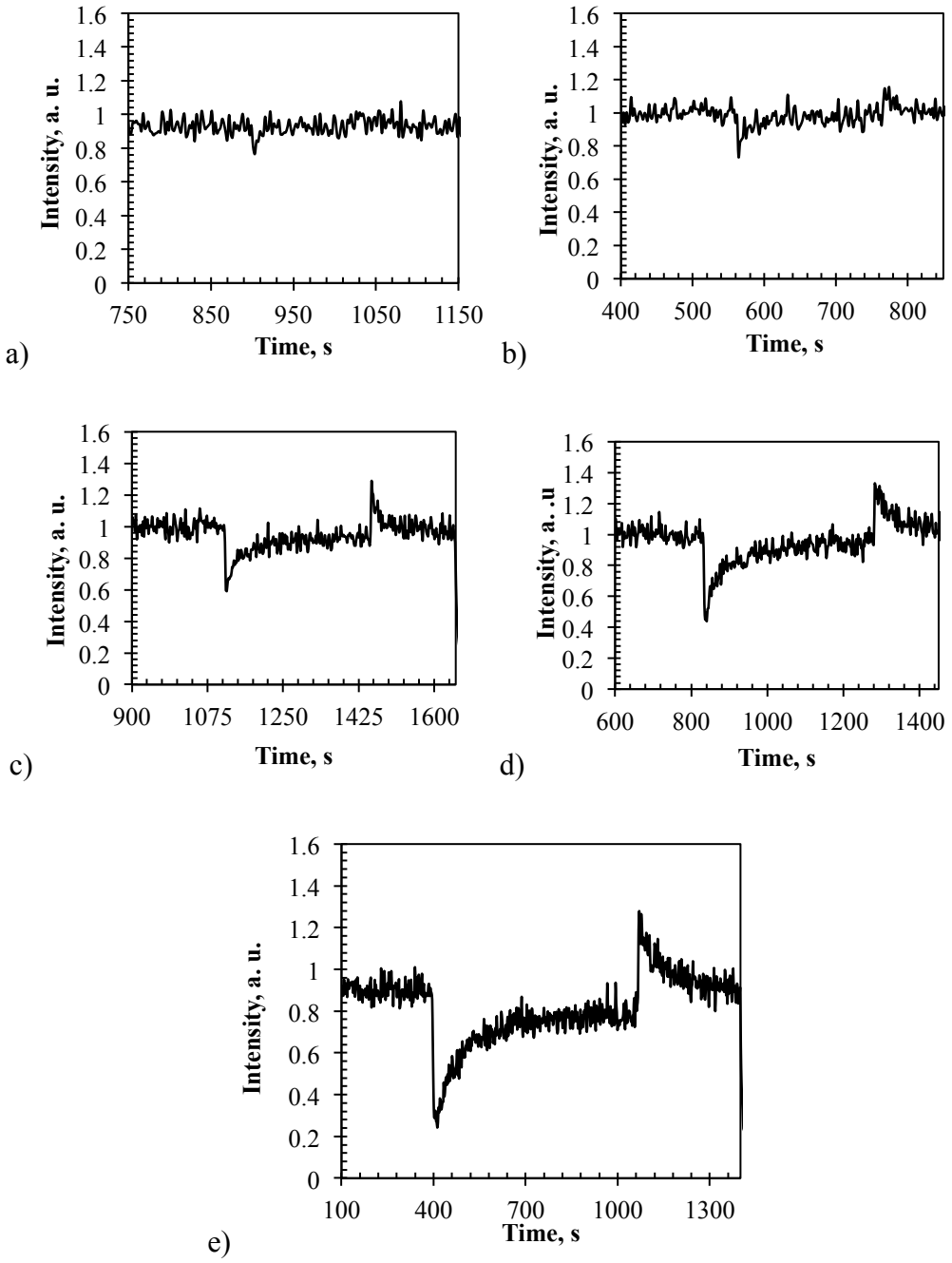


Figure 6. Normalized selected ion mass spectral profile of $[TMA]\cdot H^+$ (m/z 60) when exposed to a) 1.7 cm b) 2.7 cm c.) 3.7 cm d.) 4.7 cm e.) 5.7 cm of a 41 mg succinic acid coating respectively at 298 K and ~1.4 torr.

The heterogeneous loss in TMA signal intensity upon exposure to 1.7-5.7 cm of succinic acid is illustrated in Figure 6. In Figure 6a, the loss of TMA to 1.7 cm of succinic acid was minor. The initial exposure presented a 20% decrease in the amine signal, but there was no sign of asymptotic recovery since the signal immediately returned to the original intensity. Figures 6a-e show the increase in signal intensity with injector distance, despite the minimal uptake in Figure 6a. The signal loss in Figure 6e displays uptake features to that shown in Figure 4, but the uptake is not as pronounced with an initial decrease in amine signal of ~70%. The signal recovered for about 300 s until achieving a steady state at ~30% of the signal. Subsequent to ~300 s of steady state exposure, the moveable injector was retracted. Features showing an amine signal increase were realized followed by a gradual decline to the original intensity.

The uptake of TMA was not as pronounced initially, but the loss became more substantial as the exposure distance increased. It is likely that the exposure time for TMA of the succinic acid was not sufficient for reaction in Figure 6a. This phenomenon could be due to the increase in methyl groups inhibiting contact with the sample surface in comparison to DMA. However, with an increased exposure time, the uptake of succinic acid was dominated by irreversible loss, showing minor desorption after the injector is retracted.

Table 3. Estimated Alkylamine Uptake by Succinic Acid

	[Amine][a] ($x10^9$ molecules cm^{-3})	sample coating[b] (mg)	F_{OA}[c]
DMA	8.23±0.096	43	0.278±0.101
TMA	8.16±0.076	41	0.085±0.068

[a]Concentration of alkylamines in the fast flow reactor at ~1.4-1.6 torr. [b]Mass of acid coated to a sample tube. [c]Monolayer fraction of the organic acid layer that participated in the uptake event. The error corresponds to one standard deviation (1σ) based on 5 independent measurements on a single film.

Table 4. Estimated DMA Uptake by Organic Acid

	[Amine][a] ($x10^9$ molecules cm^{-3})	sample coating[b] (mg)	F_{OA}[c]
Succinic Acid	8.23±0.096	43	0.278±0.101
Adipic Acid	8.51±0.297	43	0.038±0.026

[a]Concentration of alkylamines in the fast flow reactor at ~1.4-1.6 torr. [b]Mass of acid coated to a sample tube. [c]Monolayer fraction of the organic acid layer that participated in the uptake event. The error corresponds to one standard deviation (1σ) based on 5 independent measurements on a single film.

In order to determine the probe depth of each alkylamine into the organic acid surface, the monolayer fractions of the acid layers penetrated as a function of amine concentration and sample size are reported in Tables 3 and 4. In Table 3, the values indicate that only about one third of a succinic acid monolayer uptakes DMA. In comparison, TMA only interacts with about 10% of the succinic acid available. Because less than a single layer of acid molecules participate in uptake, it is highly probable that the DMA and TMA molecules do not diffuse into the particle. This behavior implies that the uptake of amines by succinic acid occurs strictly on the sample surface. The differences in the values estimated for DMA and TMA is expected to be due to the number of methyl groups on each amine limiting the capacity of each to saturate the sample surface. Because TMA is larger, having three methyl groups, fewer molecules of TMA will be able to cover the surface, limiting the uptake of the gaseous amine.

Table 4 shows the difference in the probe depth of amines with respect to the identity of the acid involved. The adipic acid surface appears to uptake less than 5% of the amine molecules exposed, which is about six times less than that of succinic acid. The value determined give evidence that the properties of the acid involved may also play a role in the acid base chemistry, despite the strong basicity of the alkylamines.

3.2 Heterogeneous Kinetics

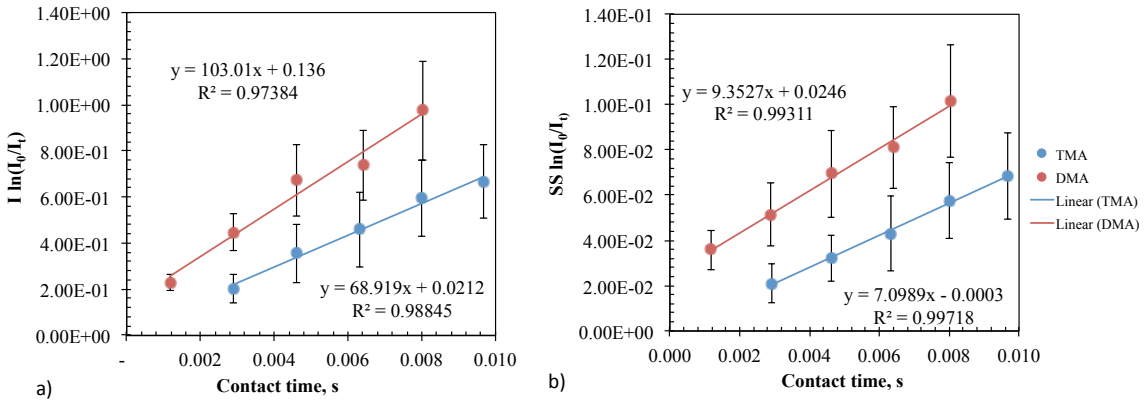


Figure 7. a) Initial and b) steady state alkylamine signal loss as a function of contact time when exposed to the succinic acid coating at 298 K and ~1.4 torr. DMA (red circles): u = 576-585 cm s^{-1}, t = 0.001-0.008 s; TMA (blue circles): u = 584-588 cm s^{-1}, t = 0.003-0.010 s.

Since the signal loss of each alkylamine increased with the injector distance, it could be assumed that the acid-base interactions are time dependent. In order to determine the rate in which the acid-base neutralization reactions occur, the amine signal loss corresponding to the initial and steady state exposure to succinic acid and adipic acid was plotted versus the exposure distance converted into a contact time. The slope of the line determined the observed first order rate constants for each reaction.

Figure 7 illustrates the initial and steady sate signal loss of DMA and TMA on succinic acid. The decays in amine signal follow first order kinetics, denoted by the linear relationship between the signal loss and time. Both the steady state and initial signal loss display dominance in reaction rate with respect to the number of methyl

groups on each amine. This suggests that the factors that control the saturation capacity of each onto the sample surface also govern the reactivity of each amine. It is assumed that the additional methyl groups limit the reactivity of the amines by causing the lone pairs on the nitrogen atom to be less accessible.

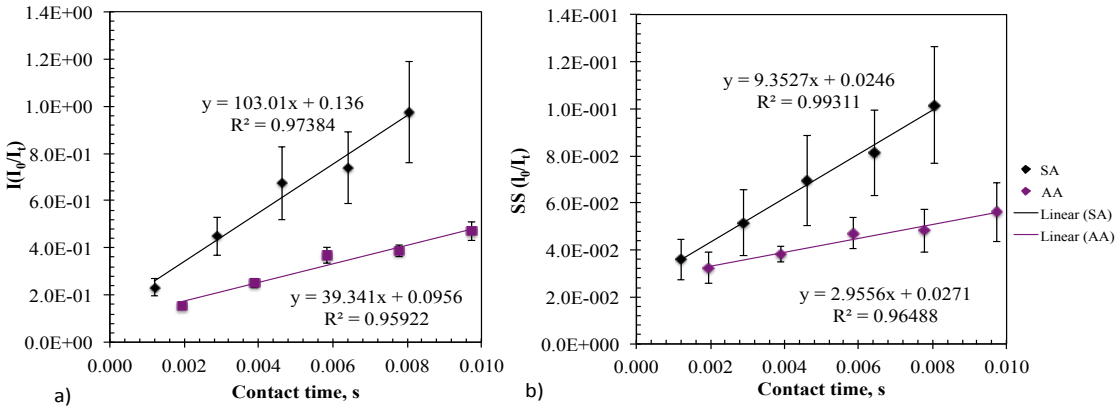


Figure 8. a) Initial and b) steady state $[DMA]\cdot H^+$ signal loss as a function of contact time when exposed to the succinic (black diamonds) and adipic acid (purple diamonds) coatings at 298 K and ~1.4-1.6 torr. DMA signal loss as a function of contact time when exposed to the adipic acid coating at 298 K and ~1.6torr. DMA: u = 514-515cm s^{-1}, t = 0.002-0.010 s.

Considering that the uptake of DMA differs between succinic acid and adipic acid, other factors beside the diffusion of the amines may play a role in the reactivity. The steady state and initial signal loss of DMA by succinic and adipic acid is depicted in Figure 8. The observed rate constants for succinic acid are about three times higher than those for adipic acid in either case. Both acids are aliphatic straight chain dicarboxylic acids (two carbon atom difference) with comparably low vapor pressures (10^{-7} torr) at room temperature. However, succinic acid has a pka_1 of 4.19, while adipic acid has a

pka_1 of 4.43. Although the physical properties of succinic acid and adipic acid are similar, succinic acid is more acidic, which causes this species to be more reactive towards DMA. Thus, the properties of the organic acids, in addition to those of the alkylamines, may influence the progress of the acid base reactions.

After applying the diffusion correction to the observed rate constants (3), the pseudo-first order rate constants were determined and utilized to calculate the steady state and initial uptake coefficients for each amine. The results fare shown in Table 5. The initial uptake is fast with average uptake coefficients of (4.92±3.68) $x10^{-3}$and (3.66±2.23) $x10^{-3}$ for DMA and TMA respectively, in addition to (1.81±0.37) $x10^{-3}$ for DMA on adipic acid (Table 6). These values denote the rapid neutralization of the succinic acid upon immediate exposure. These values estimated are comparable to the observed uptake coefficients reported for the reaction of alkylamines with citric acid: 7.31±1.13 $x10^{-3}$, 6.65±0.49 $x10^{-3}$, and 5.82±0.68 $x10^{-3}$ for MMA, DMA, and TMA respectively.[67] The rate of the acid-base reaction is also comparable to the uptake coefficient reported for the reaction of TMA with polydisperse nitric acid particles at 20% RH ($2x10^{-3}$).

[68]**Table 5. (γ_0) and (γ_{ss}) Uptake Coefficients of Amines on Succinic Acid.**[a]

	γ_{ss} ($x10^{-4}$)	γ_0 ($x10^{-3}$)
DMA	4.13±2.90	4.92±3.68
TMA	3.55±2.58	3.66±2.23

[a]The error corresponds to one standard deviation (1σ) based on 10 independent measurements for TMA and DMA respectively.

The steady state uptake was less rapid exhibiting uptake coefficients of (4.13±2.90) $x10^{-4}$ and (3.55±2.28) $x10^{-4}$ for DMA and TMA, respectively, and (1.31±1.22) $x10^{-4}$ for DMA on adipic acid. These values suggest that during the steady state exposure, much of the succinic acid surface has been saturated, which will in turn lower the reaction rate of the remaining amines. Qui et al. reported steady state uptake coefficients for MMA, DMA, and TMA on ammonium sulfate of (6.0±1.2) $x10^{-3}$, (9.4±2.2) $x10^{-4}$, and (2.3±0.4) $x10^{-4}$, decreasing with increasing methyl groups.[66] Because the reaction kinetics between dicarboxylic acids and alkylamines are comparable to those of sulfates and nitrates, which are very important components to atmospheric aerosols, neutralization of organic acids could serve as an important mechanism for the formation of particulate nitrogen in SOAs.

Table 6. (γ_0) and (γ_{ss}) Uptake Coefficients of DMA on Organic Acid.[a]

	γ_{ss} ($x10^{-4}$)	γ_0 ($x10^{-3}$)
Adipic Acid	1.31±1.22	1.81±0.37
Succinic Acid	4.13±2.90	4.92±3.68

[a]The error corresponds to one standard deviation (1σ) based on 10 independent measurements.

4. CONCLUSIONS

Interest in SOAs is continuing to increase because of the need to establish national air quality standards for fine particles, assess aerosol impacts on public health, and ascertain the affects of composition on CCN development. Although organic species are generally believed to contribute to the growth of aerosols, being found in aerosol particles of sizes as small as 10 nm atmospherically,[87,88] the identities of the species involved are poorly understood, as well as the processes leading to growth due to the complex nature of the reactions.[89,90] Because organic acids are often discovered in SOAs, acid-base neutralization by low molecular weight amines is likely to produce stable low volatility alkylaminium salt products that contribute to the growth of SOAs in addition to altering aerosol optical and hygroscopic properties.[73]

A laminar fast flow reactor coupled to an ID-CIMS was used to assess the uptake of gaseous DMA and TMA on solid phase succinic acid and adipic acid. The heterogeneous uptake of amines on each acid occurred rapidly, resulting in uptake coefficients that denote comparable reactivity to common atmospheric aerosol components. The acid-base neutralization was governed primarily by the steric effects of each amine, and the acidity of each acid. The reaction was also limited to the outermost layer of the acid coating. In addition to DMA and TMA, the heterogeneous reactions of methylamine (MA) with succinic and adipic acids respectively are needed in order to properly assess the effects of the amine basicity and steric behavior on the reaction kinetics.

Although dicarboxylic acids are classified as water soluble organic compounds, the most abundant particle phase dicarboxylic acids were reported to have deliquescence points higher than 90%, which includes succinic and adipic acid particles that have no observed deliquescence below 93% at 30°C, agreeing well with a predicted deliquescence around 99% RH.[77] Thus, dicarboxylic acids are likely to exist in aerosol particles in the crystalline phase, allowing them to serve as available sites for the uptake of atmospheric amines under dry conditions. Nonetheless, the composition of atmospheric particles can also influence salt formation by amine if stronger, or more prevalent, inorganic acids exist on the atmospheric particle.

Although amines react proficiently with organic acids, ammonia is still the dominant basic species atmospherically.[50] Unless the organic acids are directly located near amine emission sources, the neutralization reactions will occur predominantly by ammonia. However, if ammonia and exist in concentrations of the same order of magnitude as amines, alkylaminium salt formation is predicted to be the dominant mechanism.[70]

REFERENCES

(1) Seinfeld, J. H.; Pandis, S. N. *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*. 2nd ed. Wiley: New York, **2006**.

(2) Zhang, R. Y.; Khalizov, A.; Wang, L.; Hu, M.; Xu, W. Nucleation and growth of nanoparticles in the atmosphere. *Chem. Rev.* **2012**, *112*, 1957–2011.

(3) Boy, M.; Rannik Ü.; Lehtinen, K. E. J.; Tarvainen, V.; Hakola, H.; Kulmala M. Nucleation events in the continental boundary layer: long-term statistical analyses of aerosol relevant characteristics. *J. Geophys. Res.* **2003**, *108*,1-13.

(4) Poschl, U. Atmospheric aerosols: composition, transformation, climate, and health effects. *Angew. Chem. Int. Ed.* **2005**, *44*, 7520-7540.

(5) Dockery, D. W.; Pope III, C. A. Acute respiratory effects of particulate air pollution. *Annu. Rev. Public Health* **1994**, *15*, 107-132.

(6) Dockery, D. W.; Schwartz, J.; Spengler, J. D. Air pollution and daily mortality: associations with particulates and acid aerosols. *Environ. Res.* **1992**, *59*, 362-373.

(7) Laden, F.; Neas, L. M.; Dockery, D. W.; Schwartz, J. Association of fine particulate matter from different sources with daily mortality in six U. S. cities. *Environ. Health Perspect.* **2000**, *100*, 941-947.

(8) Jacobson, M. C.; Hansson, H. C.; Noone, K. J.; Charlson, R. J. Organic and atmospheric aerosols: review and state of the science. *Rev. of Geophys.* **2000**, *38*, 267-294.

(9) Myhre, G.; Shindell, D.; Bréon, F. M.; Collins, W.; Fuglestvedt, J.; Huang, J.; et al. *Anthropogenic and Natural Radiative Forcing.In: Climate Change 2013: The Physical*

Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press: New York, NY, USA.

(10) Marti, J. J.; Weber, R. J.; McMurry. P. H. New particle formation at a remote continental site: assessing the contributions of SO_2 and organic precursors. *J. Geo. Phys. Let.*, **1997** *102*, D5, 6331-6339.

(11) Kanakidou, M.; Seinfeld, J. H.; Pandis, S. N.; Barnes, I.; Dentener, F. J.; et al. Organic aerosol and global climate modelling: a review. *Atmos. Chem. Phys.* **2005**, *5*, 1053-1123.

(12) Atkinson, R. Atmospheric chemistry of VOCs and NO_x. *Atmos. Environ.* **2000**, *34*, 2063–2101.

(13) Volkamer, R.; Jimenez, J. L.; San Martini, F.; Dzepina, K.; Zhang, Q.; Salcedo, D.; et al. Secondary organic aerosol formation from anthropogenic air pollution: rapid and higher than expected. *Geo. Phys. Res. Let.* **2006**, *33*, L17811.

(14) Calogirou, A.; Larsen, B. R.; Kotzias, D. Gas-phase terpene oxidation products: a review. *Atmos. Environ.* **1998***, 33*, 1443-1439.

(15) Hallquist, M.; Wenger, J. C.; Baltensperger, U.; Rudich, Y.; Simpson, D. et al. The formation, properties and impact of secondary organic aerosol: current and emerging issues. *Atmos. Chem. Phys.* **2009**, *9*, 5155–5236.

(16) Yu, H.; McGraw, R.; Lee, S. H. Effects of amines on formation of sub-3 nm particles and their subsequent growth. *Geophys. Res. Lett.* **2012**, *39*, L02807.

(17) Wang, L.; Khalizov, A. F.; Zheng, J.; Xu, W.; Ma, Y.; et al. Atmospheric nanoparticles formed from heterogeneous reactions of organics. *Nature Geosci.* **2010**, *3*, 238–242.

(18) Zhao, J.; Levitt, N. P.; Zhang, R. Heterogeneous chemistry of octanal and 2, 4-hexadienal with sulfuric acid. *Geophys. Res. Lett.* **2005**, *32*, L09802.

(19) Zhao, J.; Khalizov, A.; Zhang, R.; McGraw, R. Hydrogen-bonding interaction in molecular complexes and clusters of aerosol nucleation precursors. *J. Phys. Chem. A* **2009**, *113*, 680–689.

(20) Krizner, H. E.; De Haan, D. O.; Kua, J. Thermodynamics and kinetics of methylglyoxal dimer formation: a computational study. *J. Phys. Chem.* **2009**, *113*, 6994–7001.

(21) Zhang, K. M.; Wexler, A. S. A hypothesis for growth of fresh atmospheric nuclei. *J. Geophys. Res.* **2002**, *107*, 4577.

(22) Khwaja, H. A. Atmospheric concentrations of carboxylic acids and related compounds at a semiurban site. *Atmos. Environ.* **1995**, *29*, 127-139.

(23) Chebbi, P.; Carlier,P. Carboxylic acids in the troposphere, occurrence, sources, and sinks: a review. *Atmos. Environ.* **1996**, *30*, 4233-4249.

(24) Kawamura, K.; Kasukabe, H.; Barrie, L. A. Source and reaction pathways of dicarboxylic acids, ketoacids and dicarbonyls in arctic aerosol: one year of observations. *Atmos. Environ.* **1996a**, *30*, 1709-1722.

(25) Kawamura, K.; Sempéré, R.; Imai, Y.; Fujii, Y.; Hayashi, M. Water soluble dicarboxylic acids and related compounds in the Antarctic aerosols. *J. of Geophys. Res.* **1996b**, *101*, (D13), 18721-18728.

(26) Ho, K. F.; Lee, S. C.; Ho, S. S. H.; Kawamura, K.; Tachibana, E.; Cheng, Y.; Zhu, T. Dicarboxylic acids, ketocarboxylic acids, a-dicarbonyls, fatty acids, and benzoic acid in urban aerosols collected during the 2006 Campaign of Air Quality Research in Beijing (CAREBeijing-2006). *J. of Geophys. Res.* **2010**, *115*, 6741-6750.

(27) Pavuluri, C. M.; Kawamura, K.; Swaminathan, T. Water-soluble organic carbon, dicarboxylic acids, ketoacids, and a-dicarbonyls in the tropical Indian aerosols. *J. of Geophys. Res.* **2010**, *115*, D11302.

(28) Kawamura, K.; Ikushima, K. Seasonal changes in the distribution of dicarboxylic acids in the urban atmosphere. *Environ. Sci. Technol.* **1993**, *27*, 2227-2235.

(29) Kerminen, V.; Teinila, K.; Hillamo, R.; Makela, T. Size-segregated chemistry of particulate dicarboxylic acids in the arctic atmosphere. *Atmos. Environ.* **1999**, *33*, 2089-2100.

(30) Hsieh, L. Y.; Chen, C. L.; Wan, M. W.; Tsai, C. H.; Tsai, Y. I. Speciation and temporal characterization of dicarboxylic acids in PM2.5 during a PM episode and a period of non-episodic pollution. *Atmos. Environ.* **2008**, *42*, 6836-6850.

(31) Miyazaki, Y., S.; Aggarwal, G.; Singh, K.; Gupta, P. K.; Kawamura, K. Dicarboxylic acids and water-soluble organic carbon in aerosols in New Delhi, India in winter: characteristics and formation processes. *J. Geophys. Res.* **2009**, *114*, D19206.

(32) Kundu, S.; Kawamura, K.; Andreae, T. W.; Hoffer, A.; Andreae, M. O. Molecular distributions of dicarboxylic acids ketocarboxylicacids and a-dicarbonyls in biomass burning aerosols: implications for photochemical production and degradation in smoke layers. *Atmos. Chem. Phys.* **2010**, *10*, 2209-2225.

(33) Sempéré, R.; Kawamura, K. Comparative distributions of dicarboxylic acids and related polar compounds in snow, rain and aerosols from urban atmosphere. *Atmos. Environ.* **1994**, *28*, 449-459.

(34) Kerminen,V.; Ojanen, C.; Pakkanen, T.; Hillamo, R.; Aurela, M.; et al. Low-molecular-weight dicarboxylic acids in an urban and rural atmosphere. *J. Aerosol Sci.* **2000**, *31*, 3, 349-362.

(35) Hatakeyama, S.; Tanonaka, T.; Weng, J.; Bandow, H.; Takagi, H.; et al. Ozone-cyclohexene reaction in air: quantitative analyses of particulate products and the reaction mechanism. *Environ. Sci. Technol.* **1985**, *19*, 935–942.

(36) Molina, M. J.; Zhang, R.; Wooldridge, P. J.; Kim, J. E.; McMahon, J. R.; et al. Physical chemistry of the $H_2SO_4/HNO_3/H_2O$ system: implications for the formation of polar stratospheric clouds. *Science* **1993**, *261*, 1418-1423.

(37) O'Dowd, C. D.; Hämeri, K.; Aalto, P.; Kulmala, M. First experimental evidence of new particle formation from organic vapours over forests. *Nature* **2002**, *416*, 497-498.

(38) Zhang, R.; Suh, I.; Zhao, J.; Zhang, D.; Fortner, E. C.; et al. Atmospheric new particle formation enhanced by organic acids. *Science* **2004**, *304*, 1487–1490.

(39) Zhang, R.; Wang, L.; Khalizov, A. F.; Zhao, J.; Zheng, J. et al. Formation of nanoparticles of blue haze enhanced by anthropogenic pollution. *Proc. Natl. Acad.*

Sci. USA **2009**, *106*, 17650–17654.

(40) Xu, W.; Zhang, R. Theoretical investigation of interaction of dicarboxylic acids with common aerosol nucleation precursors. *J. Phys. Chem. A* **2012**, *116*, 4539−4550.

(41) Smith, J. N.; Barsanti, K. C.; Friedli, H. R.; Ehn, M.; Kulmala, M.; et al. Observations of aminium salts in atmospheric nanoparticles and possible climatic implications. *Proc. Natl. Acad. Sci. USA* **2010**, *107*, 6634–6639.

(42) Hienola, A. I.; Vehkamaki, H.; Riipinen, L.; Kulmala, M. Homogeneous vs. heterogeneous nucleation in water-dicarboxylic acid systems. *Atmos. Chem. Phys.* **2008**, *9*, 1873-1881.

(43) Nadykto, A. B.; Yu, F. Strong hydrogen bonding between atmospheric nucleation precursors and common organics. *Chem. Phys. Lett.* **2007**, *435*, 14–18.

(44) Kulmala, M. How particles nucleate and grow. *Science* **2003**, *302*, 5647, 1000-1001.

(45) Xu, W.; Zhang, R. Theoretical investigation of interaction of dicarboxylic acids with common aerosol nucleation precursors. *J. Phys. Chem. A* **2012**, *116*, 4539−4550.

(46) Ball, S. M.; Hanson, D. R.; Eisele, F. L.; McMurry, P. H. Laboratory studies of particle nucleation: Initial results for H_2SO_4, H_2O, and NH_3 vapors. *J. Geophys. Res.* **1999**, *104*, 23709.

(47) Fan, J. W.; Zhang, R. Y.; Collins, D.; Li, G. H. Contribution of secondary condensable organics to new particle formation: A case study in Houston, Texas. *Geophys. Res. Lett.* **2006**, *33*, L15802.

(48) Volkamer, R.; Jimenez, J. L.; San Martini, F.; Dzepina, K.; Zhang, Q.; et al. Secondary organic aerosol formation from anthropogenic air pollution: rapid and higher than expected. *Geo. Phys. Res. Let.* **2006**, *33*, L17811.

(49) Guo, S.; Hu, M.; Zamora, M. L.; Peng, J.; Shang, D.; et al. Elucidating severe urban haze formation in china. *PNAS* **2014**, *111*, 49, 17373-17378.

(50) Ge, X.; Wexler, A. S.; Clegg, S. L. Atmospheric amines — Part I. A review. *Atmos. Environ*. **2011**, *45*, 524–546.

(51) Docherty, K. S.; Aiken, A. C.; Huffman, J. A.; Ulbrich, I. M.; DeCarlo, P. F.; et al. The 2005 study of organic aerosols at riverside (SOAR-1): instrumental intercomparisons and fine particle composition. *Atmos. Chem. Phys.* **2011**, *11*, 12387–12420.

(52) Cornell, S. E.; Jickells, T. D.; Cape, J. N.; Rowland, A. P.; Duce, R. A. Organic nitrogen deposition on land and coastal environments: a review of methods and data *Atmos. Environ.* **2003**, *37*, 2173–2191.

(53) Loukonen, V.; Kurtén, T.; Ortega, I. K.; Vehkamäki, H.; Pádua, A. A. H. et al. Enhancing effect of dimethylamine in sulfuric acid nucleation in the presence of water – a computational study. *Atmos. Chem. Phys.* **2010**, *10*, 4961–4974.

(54) Nadykto, A. B.; Yu, F.; Hakovleva, M. V.; Herb, J.; Xu, Y. Amines in the earth's atmosphere: a density functional theory study of the thermochemistry of pre-nucleation clusters. *Entropy* **2011**, *13*, 2, 554-569.

(55) Qiu, C.; Wang, L.; Lal, V.; Khalizov, A.; Zhang, R. Heterogeneous reactions of alkylamines with ammonium sulfate and ammonium bisulfate. *Environ. Sci. Technol.* **2011**, *45*, 4748-4755.

(56) Erupe, M. E.; Viggiano, A. A.; Lee, S. H. The effect of trimethylamine on atmospheric nucleation involving H2SO4. *Atmos. Chem. Phys.* **2011**, *11*, 4767–4775.

(57) Zollner, J. H.; Glasoe, W. A.; Panta, B.; Carlson, K. K.; McMurry, P. H. et al. Sulfuric acid nucleation: power dependencies, variation with relative humidity, and effect of bases. *Atmos. Chem. Phys.* **2012**, *12*, 4399–4411.

(58) Yu, H.; McGraw, R.; Lee, S.-H. Effects of amines on formation of sub-3 nm particles and their subsequent growth. *Geophys. Res. Lett.* **2012**, *39*, L02807.

(59) Lobert, J. M.; Scharffe, D. H.; Hao, W. M.; Crutzen, P. J. Importance of biomass burning in the atmospheric budgets of nitrogen-containing gases. *Nature*, **1990**, *346*, 552–554.

(60) Qiu, C.; Zhang, R. Multiphase chemistry of atmospheric amines. *Phys. Chem. Chem. Phys.* **2013**, *15*, 5738-5752.

(61) De Haan, D. O.; Tolbert, M. A.; Jimenez, J. L. Atmospheric condensed-phase reactions of glyoxal with methylamine. *Geophys. Res. Lett.* **2009**, *36*, L11819.

(62) Wang, X.; Gao, S.; Yang, X.; Chen, H.; Chen, J. et al. Evidence for high molecular weight nitrogen-containing organic salts in urban aerosols. *Environ. Sci. Technol*. **2010**, *44*, 4441–4446.

(63) Rudich, Y.; Donahue, N. M.; Mentel, T. F. Aging of organic aerosol: Bridging the

gap between laboratory and field studies. *Annu. Rev. Phys. Chem.* **2007**, *58*, 321–352.

(64) Zahardis, J.; Geddes, S.; Petrucci, G. A. The ozonolysis of primary aliphatic amines in fine particles. *Atmos. Chem. Phys.* **2008**, *8*, 1181–1194.

(65) Wang, L.; Lal, V.; Khalizov, A. F.; Zhang, R. Heterogeneous chemistry of alkylamines with sulfuric acid: implications for atmospheric formation of alkylaminium sulfates. *Environ. Sci. Technol.* **2010**, *44*, 2461–2465.

(66) Qiu, C.; Wang, L.; Lal, V.; Khalizov, A.; Zhang, R. Heterogeneous reactions of alkylamines with ammonium sulfate and ammonium bisulfate. *Environ. Sci. Technol.* **2011**, *45*, 4748-4755.

(67) Liu, Y.; Ma, Q.; He, H. Heterogeneous uptake of amines by citric and humic acid. *Environ. Sci. Technol.* **2012**, *46*, 11112−11118.

(68) Lloyd, J. A.; Heaton, K. J.; Johnston, M. V. Reactive uptake of trimethylamine into ammonium nitrate particles. *J. Phys. Chem. A* **2009**, *113*, 4840–4843.

(69) Bzdek, B. R.; Ridge, D. P.; Johnston, M. V. Amine exchange into ammonium bisulfate and ammonium nitrate nuclei. *Atmos. Chem. Phys.* **2010**, *10*, 3495–3503.

(70) Barsanti, K. C.; McMurry, P. H.; Smith, J. N. The potential of organic salts to new particle growth. *Atmos. Chem. Phys.* **2009**, *9*, 2949-2957.

(71) Qiu, C.; Zhang, R. Physiochemical properties of alkylaminium sulfates: hygroscopicity, thermostability, and density. *Environ. Sci. Technol.* **2012**, *46*, 4474−4480.

(72) Hu, D.; Li, C.; Chen, H.; Chen, J.; Ye, X.; et al. Hygroscopicity and optical properties of alkylaminium sulfates. J. *Enviro. Sci. (China)* **2014**, 26,1, 37-43

(73) Lavi, A.; Segre E.; Gomez-Hernandez, M.; Zhang, R.; Rudich, Y. Volatility of atmospherically relevant alkylaminium carboxylate salts. *J. Phys. Chem. A* **2015,** DOI: 10.1021/jp507320v.

(74) Weast R. C. *Physical constants of organic compounds. In: CRC Handbook of Chemistry and Physics.* 68th ed. CRC Press: Boca Raton, FL, **1987**.

(75) Lal, V.; Khalizov, A. F.; Lin, Y.; Galvan, M. D.; Connell, B. T.; et al. Heterogeneous reactions of epoxides in acidic media. *J. Phys. Chem. A* **2012** *116*, 6078-6090.

(76) Gomez, M. E.; Lim, Y.; Guo, S.; Zhang, R. Heterogeneous chemistry of glyoxal on acidic solutions. An oligomerization pathway for secondary organic aerosol formation. *J Phys Chem A*. **2014**, DOI: 10.1021/jp509916r.

(77) Prenni, A. J.; Demott, P. J.; Kreidenweis, S. M.; Sherman, D. E.; Russell, L. M.; Ming, Y. J. The effects of low molecular weight dicarboxylic acids on cloud formation. *Phys. Chem. A*. **2001**, 105, 11240-11248.

(78) Huang, R. J.; Li, W. B.; Wang, Y. R.; Wang, Q. Y.; Jia, W. T.; et al. Determination of alkylamines in atmospheric aerosol particles: a comparison of gas chromatography–mass spectrometry and ion chromatography approaches. *Atmos. Meas. Tech.* **2014**, 7, 2027–3025.

(79) Hall, H. K. Correlation of the base strengths of amines. *J. Am. Chem. Soc.* **1957**, *79*, 5441-5444.

(80) Fortner, E. C.; Zhao, J.; Zhang, R. Development of ion drift-chemical ionization mass spectrometry. *Anal. Chem.* **2004**, *76*, 5436–5440.

(81) Zhang, R.; Jayne, J. T.; Molina, M. J. Heterogeneous interactions of $ClONO_2$ and HCl with sulfuric acid tetrahydrate: implications for the stratosphere. *J. Phys. Chem.* **2014**, *98*, 867-874.

(82) Lelievre, S.; Bedjanian, Y.; Laverdet, G.; Le Bras, G. Heterogeneous reaction of NO_2 with hydrocarbon flame soot. *J. Phys. Chem. A*. **2004**, *108*, 10807-10817.

(83) Hanson, D. R.; Burkholder, J. B.; Howard, C. J.; Ravishankara, A. R. Measurement of OH and HO_2 radical uptake coefficients on water and sulfuric acid. *J. Phys. Chem.* **1992**, *96*, 4979-4985.

(84) Fuller, E. N.; Schettler, P. D.; Giddings, J. C. A new method for prediction of binary gas-phase diffusion coefficients. *Indust. Engin. Chem.* **1966**, *58*, 19-27.

(85) Davidovits, P.; Kolb, C. E.; Williams, L. R.; Jayne, J. T.; Worsnop, D. R. Mass accommodation and chemical reactions at gas−liquid interfaces. *Chem. Rev.* **2006**, *106*, 1323–1354.

(86) Kolb, C. E.; Worsnop, D. R. Chemistry and composition of atmospheric aerosol particles. *Annu. Rev. Phys. Chem.* **2012**, *63*, 471-491.

(87) Laaksonen, A.; Kulmala, M.; O'Dowd, C. D.; Joutsensaari, J.; Vaattovaara, P.; Mikkonen, S.; Lehtinen, K. E. J.; Sogacheva, L.; Maso, M.; Dal Aalto, P.; Petaja, T.; Sogachev, A.; Yoon, Y. J.; Lihavainen, H.; Nilsson, D.; Facchini, M. C.; Cavalli, F.; Fuzzi, S.; Hoffmann, T.; Arnold, F.; Hanke, M.; Sellegri, K.; Umann, B.; Junkermann, W.; Coe, H.; Allan, J. D.; Alfarra, M. R.; Worsnop, D. R.; Riekkola, M. L.; Hyotylainen, T.; Viisanen, Y. The role of VOC oxidation products in continental new particle formation. *Atmos. Chem. Phys.* **2008**, *8*, 2657–2665.

(88) Smith, J. N.; Dunn, M. J.; VanReken, T. M.; Iida, K.; Stolzenburg, M. R. et al. Chemical composition of atmospheric nanoparticles formed from nucleation in Tecamac, Mexico: evidence for an important role for organic species in nanoparticle growth. *Geophys. Res. Lett.* **2008**, *35*, L04808.

(89) Ehn, M.; Petaja, T.; Birmili, W.; Junninen, H.; Aalto, P.; et al. Non-volatile residuals of newly formed atmospheric particles in the boreal forest. *Atmos. Chem. Phys.* **2007**, *7*, 677–684.

(90) Wehner, B.; Petaejae, T.; Boy, M.; Engler, C.; Birmili, W.; et al. The contribution of sulfuric acid and non-volatile compounds on the growth of freshly formed atmospheric aerosols. *Geophys. Res. Lett.* **2005**, *32*, L17810.